Water permeation in carbon nanotube membranes

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Abstract:

Water treatment is one of the main battlegrounds in the world's effort to reduce greenhouse gas emission and global warming: Ever greater amounts of energy are required in developed countries to treat water to ever increasing quality standards; wastewater treatment and sea-water desalination plants are often out of reach of those developing countries that need it the most, due to high energy and capital requirements. In this opinion paper we argue that nanotube membranes have the potential to change this dynamic by lowering overall costs of filtration processes. We discuss current limitations and the latest developments towards commercialization of this technology.

1. Introduction

Water treatment is one of the main battlegrounds in the world's effort to reduce greenhouse gas emission and global warming: Ever greater amounts of energy are required in developed countries to treat water to ever increasing quality standards; wastewater treatment and sea-water desalination plants are often out of reach of those developing countries that need it the most, due to high energy and capital requirements [1*, 2]. Process integration, energy recovery and a significant improvement in the performance of polymeric membranes have steadily decreased the energy requirement of membrane-based water treatment plants (Figure 1) [3, 4]. As thermodynamics sets a floor to further decreases in the absolute energy requirements of filtration processes (ex. osmotic pressure in the case of desalination) further progress can only come from novel membrane materials capable of increasing the flux through a membrane for a given pressure difference. Although this would not decrease the amount of energy needed to produce one cubic metre of water (kWh/m^3), a higher flux can result in a smaller plant footprint, lower carbon emissions and overall lower capital costs [4].

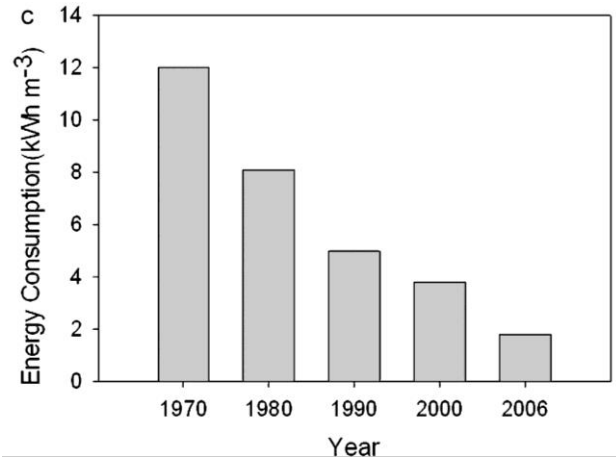

Figure 1. Change in power consumption for the reverse osmosis stage in seawater RO plants from the 1970s to 2006. Reproduced from [4].

The ultra-high water flow rates first observed in carbon nanotubes (CNTs) in the early 2000s have generated hope that CNTs could be the perfect material to produce membranes with fluxes orders of magnitude higher than commercial polymeric ones [4, 5]. This initial work investigating flow in individual nanotubes or small membranes, either experimentally or via molecular dynamics (MD), has, more recently, given way to studies focussing on the fabrication of CNT membranes using methodologies with potential for large-scale manufacturing. This transition, though, has, so far, yielded much smaller performance improvements that what the initial studies promised. For example, a 4-fold increase in flux, compared to a normal thin film composite (TFC) polyamide membrane, has been obtained when CNTs with random orientation have been incorporated in the membranes' active layer (Figure 2) [6*]. This is only a small fraction of the orders-of-magnitude enhancements observed for pure water flow in CNTs. The addition of the CNTs produced no change in salt rejection as this is still determined by the polymer. In fact the tubes' are fully embedded in the active layer and do not have direct access to the external environment. Essentially the act as internal fast lanes for water molecules once the water has already penetrated the polymer surface.

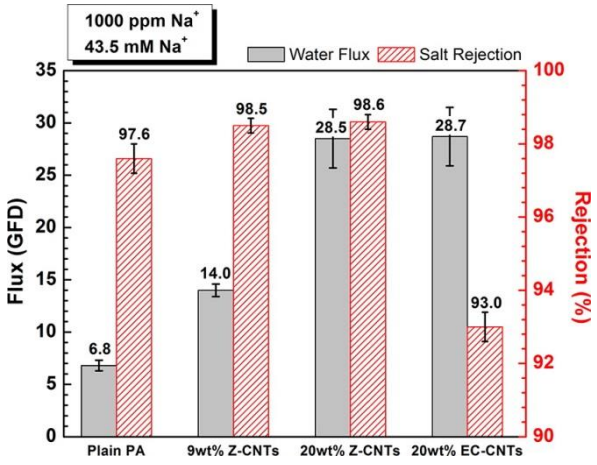

Figure 2. Water flux (solid) and salt rejection (hatched) as a function of CNT concentration in the selective layer of a PA nanocomposite membrane; reprinted with permission from [6].

To date there is only very limited commercial use of nanotube-based membranes. This can be attributed mainly to a twin set of challenges, one regarding the fundamental understanding the effect on flow of nanoscale confinement and how it can be controlled effectively and the other concerning the development of fabrication methods for nanotube membranes that can be scaled to a level capable of competing with commercial membranes.

2. Challenges in the fundamental understanding of water permeation through nanotubes

The first results showing pure water flow in carbon nanotubes up to 50,000 times higher than what is predicted by classical fluid dynamics were greeted with some justified degree of skepticism [5]. The amount of experimental (Table 1) and modeling [7*, 8*] evidence has now settled those initial doubts, with the increase in flow defined as the flow enhancement compared to an equivalent no-slip Poiseuille flow [9]. The large variability in flow enhancement and permeability values observed, though, points to the fact that the small membrane sizes used and uncertainty over nanotube diameter distribution can result in significant errors, making direct comparison with commercial membranes challenging. In addition, selectivity has to be considered when evaluating the overall performance of a membrane [10*].

Table 1. Selected experimental values for pure water flow enhancement and permeability in CNT membranes, as a function of CNT diameter.

Ref.	CNT Diameter (nm)	Flow enhancement	K (10^{-10}m^{3}m^{-2}s^{-1}Pa^{-1})	Remarks
[11]	0.81-1.59	51-882	0.1	single tube experiment
[12]	1.3-2.0	560-8400	2-8	VA-CNT membrane
[13]	7	10^4-10^5	10	VA-CNT membrane
[14]	10	5 x 10^5	64	4 mm long CNTs
[6]	10	-	0.4	PA/CNT-TFC membrane
[15]	44	34	25-100	non-graphitic CNT structure
[16]	200-300	~1	-	no enhancement obs.

While a full understanding of the origin of the flow enhancement in CNTs has not yet been reached, some aspects are now generally accepted: The presence of a ~2 nm size threshold for nanotube diameters below which continuum modeling - based on averaging and conservation laws - can no longer be used and the individual molecular interactions have to be necessarily taken in account [17]. For such small tubes, in the reverse osmosis and nanofiltration ranges, molecular dynamics is the tool of choice to model experimental results. MD can additionally provide insight on specific aspects of the effect of nanoscale confinement on flow that cannot be evaluated otherwise. These include the water molecules'

dipole orientation [7, 18] or the formation of complex conformations [19], both of which are predicted to have significant effects on the resulting flux. MD, though, suffers from uncertainty on the exact nature and value of the interaction parameters used to describe the fluid and tube walls [20**] [21]. In addition, cut-off of specific interactions (in particular long-distance electrostatic ones) can significantly alter the flow predictions, adding some uncertainty to results in the literature [7, 22]. The increase in computational power has now made possible simulating tubes with characteristics closer to the real material, providing novel insights in the flux-tube structure relationship. These include flux reductions induced by the presence of defects on the tube's surface [23] and by entrance effects [8] - in analogy to what observed at the macroscale. The understanding of entrance effects at the nanoscale, in particular, remains challenging with both theoretical [24] and experimental [25] approaches providing some insight. Flux can be further decreased or increased by selective functionalization of the nanotube tips [26**, 27].

As high fluxes have been observed also in CNT membranes in the nanofiltration/ultrafiltration regime, continuum models have also been developed. Most are based on confinement effects on flow and slippage due to reduced fluid mobility or variable viscosity. The inclusion of fluid slip at the tube's wall, in particular, is the result of MD observations showing that the classical no-slip hypothesis cannot be applied for water flows in CNTs. Therefore, a conservation law is assumed at the boundary, the Navier condition, which depends only on a length parameter that is referred as slip length [28]. In [29*] a general model for the calculation of the slip length has been proposed by the authors of the present work within the continuum model (for tubes with diameter above the 2 nm threshold). The expression derived for the flow enhancement relies on statistical thermodynamics to obtain an expression for the fluid velocity at the wall as a function of the strength of the solid-liquid molecular interactions, and is capable of explaining the large variability in experimental and modeling results observed in the literature (Table 1) [29, 30]. For example, the lower flow enhancement observed in [15] can be attributed not only to the larger diameter but also to the tubes' structure which, due to the synthesis technique, is quasi-amorphous and rich in functional groups. In [31] an alternative expression for the boundary conditions is derived via the so-called second gradient theory for continuum mechanics starting from the Navier-Stokes equations. Other models considering a different viewpoint are also available, focusing on the effects of compressibility [32, 33], friction [34] or shear stress dependent viscosity [35, 36] on flow. In particular, a variable viscosity along the tube's radius has been postulated via MD [37]. This concept has been used to explain the flow enhancement, assuming a 2-phase liquid in the tube with a constant and reduced value in an annular region close to the wall [38]. In contrast, [30] developed a continuous expression for the viscosity variation along the radius. The former approach implies that there is an upper limit to the flow enhancement value that can be obtained. While other MD results seem to suggest the presence of a maximum for the flow enhancement [7, 8], the very validity of the model in [38] has been recently called into question [39].

3. Towards the industrialization of carbon nanotube membranes

The flow enhancement values observed in carbon nanotubes membranes (Table 1) have stimulated a strong interest in developing large-scale, highly permeable membranes, in the ultrafiltration, nanofiltration and reverse/forward osmosis domains [40]. Interestingly, if one compares literature values in terms of permeability to a typical TFC membrane, the results appear to be less than stellar (Table 1). For example the seawater permeability of the PA-

TFC membrane in Figure 2 is about $0.1*10^{-10}$ m^3 m^{-2} s^{-1} Pa^{-1} with no CNTs [6]. The addition of nanotubes (average diameter 1.5 nm) generates about a 4-fold increase, which well compares with the seawater permeability for a CNT membrane (diameter 1 nm) obtained via MD [26]. Although these values are roughly 10 times higher than the permeability of a typical commercial polymeric RO membrane (Filmtec SW30HR-380, [41]), salt rejection is significantly lower, leaving the edge with the commercial one. It is important to notice that salt rejection in CNT membranes in MD simulations and in commercial polymeric RO membranes follows a fundamentally different mechanism: In the former case, this is based primarily on size exclusion, therefore requiring very small tubes. In polymeric ones, the main mechanism is solution-diffusion through the porosity of the membrane. In addition, there is a strong interaction between the solutes in the feed and the organic functional groups in the RO membrane active layer. A potential combination of the two mechanisms has been hypothesized in a MD paper, where functional groups were attached to the tip of a CNT to enhance salt rejection [26].

3.1 Vertically aligned CNT membrane

Vertically align CNT (VA-CNT) membranes were the first to be fabricated for water permeation experiments (Figure 3a). These small membranes (effective filtration area ~1 cm^2) were produced by infiltrating the non-permeable matrix material into the gaps of a nanotube array grown by chemical vapour deposition (CVD) on silicon wafers or similar substrates [12, 13, 42]. These membranes and more recent ones [14*] can be categorised as vertically aligned CNT (VA-CNT) membranes (Figure 3a). The filling material (a polymer or inorganic material) is dense and, therefore, the porosity of VA-CNT membranes solely consists of the inner tube of CNTs, allowing to fully capitalizing on the observed flow enhancement effect. The higher the density of the initial CNT forests, the higher the overall membrane performance, provided that the matrix materials can still be infiltrated around the tubes [43].

While VA-CNT membranes are promising in term of permeability, selectivity remains a problem, in particular for desalination. A VA-CNT membrane (CNT average diameter 1.6 nm) reached 40-60% ion exclusion efficiency for a 1 mM potassium chloride solution [44], similar to a commercial nanofiltration membrane, However, this rejection is dominated by the Donnan exclusion mechanism and the rejection drops to nearly zero when the KCl concentration increased to only 10 mM. Seawater normally contains a much higher salt content, above 0.5 M, and, as discussed, commercial RO membranes can reject over 99%. For effective salt rejection, CNTs with sufficiently small diameter, 0.49-0.59 nm according to a MD study [45], could provide sufficient steric hindrance to achieve higher than 95% sodium chloride rejection. Steric exclusion is also especially effective in excluding neutrally or weakly charged compounds, such as active pharmaceutical ingredients and boron. Such small diameters, though, are extremely difficult to achieve at any scale.

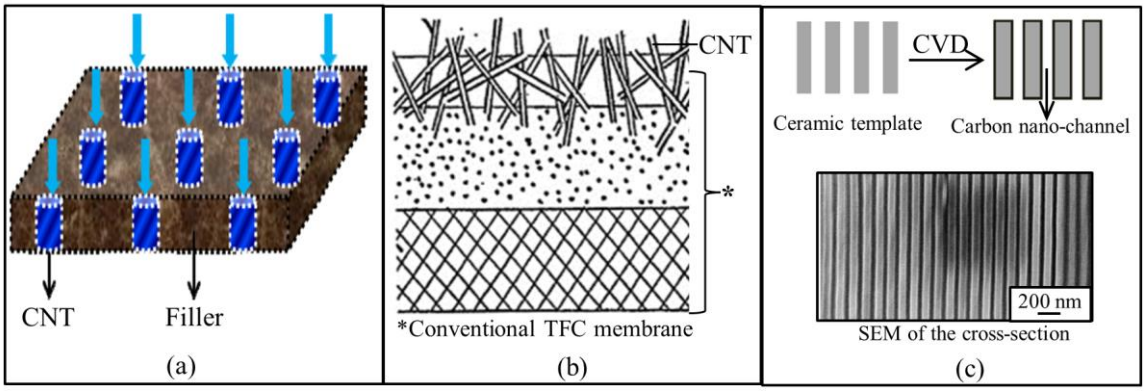

Figure 3. Schematics of CNT membranes: (a) VA-CNT (reprinted with permission from [46]), (b) TFC-CNT [47] membranes (c) templated CNT membranes [13].

3.2 Thin film composite CNT membranes

To overcome the selectivity and scale-up problems associated with VA-CNT membranes, CNTs can be incorporated into state-of-the-art polymeric membranes. The nanotubes can be embedded into conventional thin film composite membranes by blending CNTs in to the reactant solution before interfacial polymerisation (Figure 3b) [4]. With this method, due to the relatively lower CNT content and also their random orientation, the flow enhancement effect can only be partially exploited (Figure 2). In a patent filed by NanOasis Inc. [47], where 0.8 nm single wall CNTs (SWCNTs) were used to make TFC-CNT membranes, the flux was doubled with a promising salt rejection of 97.69% using synthetic seawater. However, this increase has been attributed to the presence of ‘nanocorridors’ between the external surface of CNTs and the crosslinked polymeric matrix [48]. The nanocorridors are low resistant nanogaps which serve to enhance the water transport by allowing water molecules to penetrate faster along the gaps.

Compared to VA-CNT membranes, TFC-CNT membranes are significantly closer to commercialization, albeit with a lower overall performance (Table 1). Despite this achievement, further significant advancements can be obtained by increasing the density of CNTs [26] and improving their vertical alignment. In particular, the latter will require extensive work to study the interfacial interaction with the polymer solution during membrane formation, also in relation to the effect on the presence of the cited ‘nanocorridors’.

3.3 Templated CNT membranes

As shown in Figure 3c, a third alternative is to use ceramic membranes as templates for the deposition of carbon via chemical vapour deposition (CVD), with a conformal carbon coating formed on the walls of the pores of the template [9]. This solution eliminates any nanotube alignment problem and is scalable [49], though suffers from some of the same limitations of other ceramic membranes [4]. A recent publication has used polyethylene shopper bags as the carbon source for the deposition process, addressing its sustainability, something rarely considered in this field [50].

4. Outlook and perspective

The very high flow enhancement values measured in carbon nanotubes have not yet translated in carbon nanotube membranes with equally high fluxes. Nonetheless, intense research and development on carbon nanotube membranes continues with significant industrial involvement.

Although the quest for flux increases has dominated research and development in the field of carbon nanotube membranes, these materials have other promising properties that could further increase the efficiency and reduce the cost of water treatment. For example, fouling is estimated to account for 20-30% of operating cost of seawater desalination [2]. CNTs have been found to have antibacterial properties, preventing the growth of biofilms [51]. In addition, due to their high electrical conductivity, simple and effective electrochemical methods could be used to remove fouling from CNT membranes [52].

Another example is given by a radical departure from the approaches discussed so far, where a CNT membrane has been used as an effective salt sorbent from a saline feed. In this membrane the CNTs are spread flat on the substrate, thereby by-passing all nanotube alignment and fouling or concentration polarization issues [53].

The convergence of ever more powerful molecular dynamics and a better understudying of the effect of nanotube characteristics on permeation and selectivity point to the fact that high flux carbon nanotube membranes can become a valid competitor for current commercial nanofiltration and RO polymeric ones, provided that more cost-effective fabrication methods can be developed.

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